BUSINESS CONFIDENTIAL PROJECT REPORT

CONTINUOUS PROCESS FOR THE PRODUCTION OF SILANE ESTERS

Preliminary Laboratory Study of the Cyanoethyltriethoxysilane System

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SUMMARY

Preliminary investigation has shown that cyanoethyltriethoxysilane can be produced continuously by mixing cyanoethyltrichlorosilane with ethanol and feeding the mixture directly into a thin film evaporator to remove hydrogen chloride and excess alcohol. The product is then neutralized, filtered and distilled in subsequent steps. Evaluation of other materials, as well as CNE, in a pilot reactor, which could be of lab scale, is necessary before adequate information can be provided for the design of a production unit. In addition to the possibility of increased yields due to shorter times under acidic reaction conditions, the installation of a production unit should greatly reduce the cost associated with materials handling in the multi-step batch process now employed.

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INTRODUCTION

The development of a continuous process for the production of silane esters, particularly trimethoxysilane, was initiated during late 1966.[1] A key step in the resulting process is the separation of the product from partially esterified chlorosilanes. While this process is applicable to the more volatile materials, it is not suitable, as it stands, for production of high boiling esters, such as β-cyanoethyltriethoxysilane (CNE). This report describes the preliminary laboratory development of a continuous esterification process applicable to high boiling esters, such as CNE.

Reaction Considerations

β-Cyanoethyltriethoxysilane (CNE) is hydrogenated to produce γ-aminopropyltriethoxysilane (A-1100). The reactions and conditions, starting with acrylonitrile and trichlorosilane to prepare A-1100, are:

I. $CH_2 = CH\,C{\equiv}N + HSiCl_3 \xrightarrow[\text{Tripropylamine}]{5\%} N{\equiv}C\,CH_2CH_2SiCl_3$

acrylonitrile; trichlorosilane; β-cyanoethyltrichlorosilane (CNT)

II. $CNT + C_2H_5OH \xrightarrow{1,2,3,4} N{\equiv}C\,CH_2CH_2Si(OC_2H_5)_3$ (CNE)

1. Alcoholysis (esterification) (60-120°C, 40-120 mm Hg.)
2. Neutralization ($\equiv SiCl + H_2NCH_2CH_2NH_2 + C_2H_5OH \longrightarrow \equiv SiOC_2H_5 + HCl{\cdot}H_2NCH_2CH_2NH_2$)
3. Distillation (225°C, 30 mm Hg.) (Arochlor, Chaser)
4. Filtration

III. $CNE + H_2 \xrightarrow{5,6,7} NH_2CH_2CH_2CH_2Si(OC_2H_5)_3$

γ-aminopropyltriethoxysilane (A-1100)

5. Hydrogenation (150°C, 600 psi) (Ni catalyst)
6. Filtration (Ni catalyst removal)
7. Distillation (225°C, 30 mm Hg.) (Arochlor, Chaser)

The most important side reaction, the alcoholysis - hydrolysis of the nitrile group to produce the organic ester, occurs during the esteri-

fication step.

IV. $\equiv SiCH_2CH_2C\equiv N + H_2O + C_2H_5OH \longrightarrow SiCH_2CH_2C(=O)-O-C_2H_5 + NH_3$

The water required in this reaction is believed to be produced by another side reaction, the hydrogen chloride reaction with ethanol to produce ethyl chloride and water.

V. $C_2H_5OH + HCl \longrightarrow C_2H_5Cl + H_2O$

Hydrolysis of silanic chloride and/or ethoxide to produce siloxane heavies also consumes a portion of the water produced in the above reaction.

VI. $2\ \equiv SiX + H_2O \longrightarrow 2HX + SiOSi$

(x = Cl or C_2H_5O)

In another side reaction, the organic ester reacts with the amine produced during hydrogenation to form an amide.

VII. $(C_2H_5O)_3Si(CH_2)_3NH_2 + (C_2H_5O)_3Si(CH_2)_2C(=O)-O-C_2H_5$

$\longrightarrow (C_2H_5O)_3Si(CH_2)_3NHC(=O)(CH_2)_2Si(OC_2H_5)_3 + C_2H_5OH$

In addition, the tripropylamine catalyst used in the silane-olefin addition reaction, and the ammonia produced by nitrile hydrolysis, as well as, the ethylene diamine used for neutralization react with hydrogen chloride to produce amine hydrochlorides. Finally, an unknown "acidic" material, as well as, polymer heavies and silicon-tetrachloride is produced during the silane-olefin addition.

Process Considerations

The current CNE process includes:

1) Continuous reaction of trichlorosilane and acrylonitrile in a tubular reactor in the intermediates area.

2) Transfer of the crude CNT to storage.

3) Transfer of the crude CNT to polymers.

4) Batch reaction of CNT with ethanol.

5) Neutralization of residual acid with ethylene diamine.

6) Filtration of amine hydrochloride salts.

7) Transfer of crude CNE to storage.

8) Transfer of crude CNE to monomers.

9) Distillation.

10) Transfer of pure CNE back to storage, where it is held for hydrogenation to A-1100.

The proposed continuous unit would carry out the same reaction sequence continuously in a train of components including: a continuous still for CNT, a chlorosilane-ethanol reactor, a neutralizer, a filter, and a product still. This process is expected to yield a higher recovery of chlorosilane as product, as well as reduce costs, such as those assigned to overhead for handling and storage of material.

DISCUSSION

The chlorosilane-alcohol reaction (I) appears to be quite rapid, while the organic ester producing reaction sequence (IV and V) is relatively slow. A "mixing tee" reactor, followed closely by a thin film evaporator for removal of excess ethanol and hydrogen chloride, allows adequate time for the chlorosilane reaction, but these same conditions are unfavorable for the organic ester formation. Experiments show greater than 90% of the chlorosilane (> 97% of the SiCl) converted to product in the laboratory unit with a very short contact time (<15 Min.). The organic ester content is < 1% as opposed to batch operations where the normal range is >2%. Any reduction in organic ester formation results in a double savings of product since loss of product to the amide (VII) after conversion to A-1100 is a function of carboxylic ester content.

The chloride content of material from the laboratory continuous unit ranged from 5-13% at atmospheric pressure. Slight reduction of pressure to 500 mm Hg. resulted in a material containing < 0.5% chloride. Since there was no liquid seal in the line from the evaporator to the product receiver, hydrogen chloride which had once been evaporated was free to redissolve in the product. It is not yet clear if the use of reduced pressure is necessary in a properly designed reactor.

The acid content (reported as Cl^-) of CNE prepared from undistilled CNT in both laboratory and production equipment is normally 3 + 2%, while the chloride due to unreacted CNT is less than 0.5%. Elimination of this unknown acidic material, as well as, silicon tetrachloride (which reacts with alcohol to produce tetraethylsilicate), and tripropylamine (which reacts with hydrogen chloride to produce amine hydrochloride) makes the use of distilled CNT in a continuous unit attractive if not imperative. Continuous

distillation of crude CNT in the laboratory wiped film unit produced a satisfactory product and failed to show any unusual problems in handling low boilers or residue, although the residue does become viscous when cold and exposed to air. The product melting point is 36°C.

Although ethylene diamine has been used for some time as the neutralizing agent for the production of CNE, it has some undesirable properties. Ethylene diamine and its vapor are corrosive to skin, while the hydrochloride is corrosive to steel equipment, as well as difficult to filter. Use of ethanol solutions of sodium ethoxide was not attractive in the batch process due to loss of pot yield from the large volume required. The commercial availability of sodium ethoxide solutions, the possibility of recycling ethanol and a de-emphasis of the concept of pot yield, make sodium ethoxide the preferred neutralizing agent in the continuous unit.

CONCLUSIONS AND RECOMMENDATIONS

Installation of a continuous esterification unit in close proximity to the intermediates CNT reactor should increase the conversion of chlorosilane to product, as well as reduce the handling required by the current process. However, this study represents only a preliminary process definition. It is recommended that a pilot unit, either labotatory or pilot plant scale, be used to obtain adequate data for proper design of a production unit. This apparatus should also be used to define modifications of the system for production of phenyl triethoxysilane (A-153), vinyl tris(β-methoxyl-ethoxy)silane (A-172), and γ-methacryloxypropyltrimethoxysilane (A-174). It is also recommended that a study be made of the possibility of incorporating a fixed catalyst bed hydrogenation unit into the CNE system to permit complete continuous processing to A-1100.

Use of the same equipment for production of A-174 and A-1100 should be attempted with caution since A-1100 and hydroquinone, the polymerization inhibitor used in A-174, react to produce a highly colored material which could cause discoloration of either product if cross contamination occurred.

EXPERIMENTAL

A comparison of the product properties and reaction conditions of distilled and crude CNT was made by preparing batch samples of CNE. Experiment 1, Table I, represents the sample prepared from crude CNT. In this experiment 138 g of ethanol was added to 188 g of cyanoethyl-trichlorosilane (as produced in the intermediates reactor) at 60-70°C, 30 mm Hg. over a period of 2 hours. Lites (22 g) consisting primarily of trichlorosilane, silicon tetrachloride and their esters were trapped from the vent. Chromatographic analysis of the remaining product (197 g) showed 11.6% residual alcohol, indicating that stoichiometric excess had been added.It is also of significance that sodium hydroxide titration showed 4.5% acid calculated as Cl^- while no chlorosilanes were detected by chromatograph. This chloride would be equivalent to slightly

greater then 30% mono-chloro ester. Experiment 2, Table I, represents the material made with distilled CNT. In this experiment 154 g (3.3 moles, 10% stoichiometric excess) of SD2B was added to 188 g of distilled cyanoethyltrichlorosilane at 60-90°C, 35-50 mm Hg. over a period of 2 hours. Chromatographic analysis again showed residual alcohol (7.6%) indicating a stoichiometric excess. Again chlorosilanes were not detected. However, titration indicated a ten fold decrease in acid content to 0.4%.

Although the organic ester, β-carbethoxyethyltriethoxysilane, is present in production batches of CNE, the concentration in laboratory preparations has been very low or non-existent. In order to determine effect of time on organic ester formation, a sample of CNE was analyzed 7 minutes after preparation in the laboratory continuous unit. Analysis of the same sample 3 1/2 hours later showed a 350% increase in organic ester content and a decrease in product and chlorosilane content (Table II). This shows that the rate of organic ester formation is quite slow relative to chlorosilane esterification, which was complete before the first analysis.

A laboratory unit was assembled from a 6 mm teflon tee, an ASCO Rota Film evaporator and a feed system consisting of 2 pressure teflon bottles and flowmeters. This apparatus was used to determine the feasibility of the continuous process. Experiment 1, Table III, which will serve as a batch control, was carried out by adding 154 g ethanol to 188 g distilled CNT at 60-90°C, 35-50 mm Hg. Experiments 2 through 5, Table III, were run with variations in ratio of alcohol to chlorosilane, and temperature. Conversion of CNT to CNE ranged from 70% to 93%, which corresponds to a conversion of chloride to alkoxy of 89% to 98%. Chloride content was much higher than can be attributed to silanic chloride. Experiments 6 and 7 represent tests at lower pressure. No effect was noted when the pressure was reduced to 650 mm Hg. However, at 500 mm Hg. the acid content was 0.43% as in the control sample. Conversion of chloride to product was 99%.

The experiments in Table IV represent a comparison of ethylene diamine and sodium ethoxide neutralization. A sample of CNE, having the properties shown, from the production kettle was split and neutralized with either ethylene diamine or sodium ethoxide solution in ethanol. Following 0.1μ filtration, the samples were analyzed by GCA. No differences were seen, in these experiments, between sodium ethoxide and ethylene diamine as a neutralizing agent for CNE.

BIBLIOGRAPHY

1. Project Report - R. P. Boersma; to be issued April 1968 - "Continuous Process for Low Boiling Silane Esters Trimethoxysilane"

NOTEBOOK REFERENCES

PD 1350; PD 1411

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Attachments

TABLE I

EFFECT OF CNT PURITY ON CHLORIDE CONTENT OF CNE

Experiment	1	2
Reference N. B.	1350-89	1411-4
	Crude CNT	Distilled CNT
Conditions		
Weight of CNT	188 g	188 g
Weight of EtOH	138 g	154 g
Reaction time	2 hr.	2 hr.
Temperature	60-90°C	60-90°C
Pressure	40 mm Hg.	35-50mm Hg.
Product Properties		
Cl^- (by NaOH)	4.5%	0.43%
ClCNE[1]	N. D.	N. D.
CNE[2]	78.6%	88.6%
% alcohol	11.6%	7.6%

TABLE II

CARBOXYLIC ESTER FORMATION VS. TIME

Reference N. B. 1411-14

Conditions

Time after reaction	7 min.		3 2/3 hr.	
Temperature	25°C		25°C	
Composition				
	Wt. %	Moles/100 g	Wt. %	Moles/100 g
Cl CNE[1]	1.4	0.0068	1.1	0.0053
CNE[2]	51.4	0.237	43.7	0.202
C = O[3]	0.9	0.0034	3.1	0.012

[1]ClCNE: cyanoethyldiethoxychlorosilane

[2]CNE: cyanoethyltriethoxysilane

[3]C = O: carbethoxyethyltriethoxysilane

TABLE III

EFFECT OF OPERATING CONDITIONS ON PROPERTIES OF ESTERS PREPARED IN THE LABORATORY CONTINUOUS UNIT

Experiment	1	2	3	4	5	6	7
Reference N. B.	1411-4	1411-7	1411-7	1411-7	1411-7	1411-14	1411-14
	Control	Alcohol/Silane Ratio and Temperature Variation				Reduced Pressure	
Conditions							
Temperature	60-90°C	90-95	135	135	95	95	95
Pressure mm. Hg.	35-50	Atm.	Atm.	Atm.	Atm.	650	500
Ratio $\frac{\text{Moles Alc.}}{\text{Moles CNT}}$	3.3/1	4.5/1	4.5/1	6.6/1	6.6/1	4.5/1	4.5/1
Composition							
Cl^- %	.43	10.4	12.9	6.6	5.4	7.5	.43
ClCNE %[1]	N. D.	5.9	23.9	13.2	2.0	1.6	1.4
CNE %[2]	88.6	60.7	56.1	69.8	50.7	49.5	51.4
C = O %[3]	.2	.1	.3	.6	.8	2.1	.9
Conversion	----	90%	71%	82.5%	93%	97%	97%

[1] ClCNE: cyanoethyldiethoxychlorosilane

[2] CNE: cyanoethyltriethoxysilane

[3] C = O: carbethoxyethyltriethoxysilane

TABLE IV

NEUTRALIZATION OF RESIDUAL CHLORIDE IN CYANOETHYLTRIETHOXYSILANE

Experiment		1	2
Reference (Notebook 1350-80)			
Neutralizing Agent	(Initial Composition)	EDA[4]	NaOEt
		Composition	
Acid (Cl^-)	(1.1%)	N. D.	N. D.
Ethanol	(5.8%)	2.2%	28.3%
CNE[1]	(67.2%)	71.3%	59.1%
CNE adjusted[2]	(80.5%)	82.1%	85.8%
C = O adjusted[3]	(2.2%)	2.1%	2.2%

[1]CNE: cyanoethyltriethoxysilane.

[2]Adjusted to account for dilution due to alcohol.

[3]C = O: carbethoxyethyltriethoxysilane.

[4]EDA: Ethylene diamine.